The invention relates to a process for the production of metal salts of trifluoromethane sulphonic acid by reacting trifluoromethane sulphonic acid with a metal alcoholate and their use as esterification catalyst and/or transesterification catalyst for the production of hydroxycarboxylic acid esters.

Trifluoromethane sulphonic acid (CF_3SO_3H) is one of the strongest organic acids. Its protonation power is stronger than that of sulphuric acid. Its metal salts, i.e. metal perfluoromethane sulphonates, also called metal triflates, are available as solids or in solution.

The most frequent fields of application of metal compounds of trifluoromethane sulphonic acid are their use as catalyst in the polymerisation of aromatic alkenes, of aromatic monomers, in electrophilic polymerisation of 1,3-pentadiene, the cationic ring opening polymerisation of tetrahydrofuran, in the Michael reaction of O–silylated ketene acetals with alpha,beta-unsaturated esters. Further fields of application are aldol and Friedel-Crafts reactions.

From US 4,219,540, the production of metal salts of trifluoromethane sulphonic acid and their use in antiperspirants is known. The aluminium salt of trifluoromethane sulphonic acid is produced by adding trifluoromethane sulphonic acid at room temperature to an aqueous suspension of barium carbonate and stirring the mixture, filtering it and removing water from it at reduced pressure and elevated temperature and drying it.

The barium trifluoromethane sulphonate thus obtained is again dissolved in water, stirred and aluminium sulphate dissolved in water is added at room temperature. After heating, filtration is carried out and the filtrate is decolorised with carbon, filtered once more and water is driven off at reduced pressure and elevated temperature, and it is dried. In a similar manner, the corresponding triflates have been produced for the rare earth metals Ce, La and the Nd-Pr alloy didymium [neodymium-praeseodymium-alloy].

A disadvantage is the complicated recovery of the metal triflate and the low yield with respect to the trifluoromethane sulphonic acid used.

In comparison with the process described above, the production process according to the invention leads, among other things, to the following improvements:

- simpler synthesis,
- high yields,
- no formation of salts as waste-producing products and
- higher purity with respect to foreign metal ions since no foreign metal compounds are used for the synthesis.

Thus, the following purities are independently of each other obtainable for the aluminium triflates/aluminium alcoholate triflates according to the invention

for Na and Fe, less than 100 ppm respectively
for Ba, Pb, Ni, Ti, Va and Zn, less than 10 ppm respectively
for As, Co, Hg, Mn, Sb, Se, Sn and Ta, less than 1 ppm respectively

The object of the invention is achieved by way of a process for the production of metal salts of trifluoromethane sulphonic acid by reacting trifluoromethane sulphonic acid CF_3SO_3H with a metal alcoholate, if necessary in a solubiliser/diluent at a temperature of -40 °C to +100 °C, preferably 0 °C to 80 °C, the metal (M) being Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Sc, Y, La, Ti, Zr, Fe, Cu, Ag or Zn, preferably Al, Ti or Zr, and the alcoholate group(s) of the metal alcoholate exhibiting 1 to 28 carbon atoms, preferably 2 to 8 carbon atoms, based on one group, as well as, optionally, furthermore the following: hydroxy groups (C-OH), ether bonds (C-O-C) and/or more than one alcoholate bond (M-O-).

According to the invention, metal triflates (metal salts of trifluoromethane sulphonic acid) are compounds which exhibit at least one trifluoromethane sulphonic acid group.

Apart from at least one acid group, the metal triflate can also exhibit one alcoholate group with 1 or 2 bonds (2-dentate ligand) with the metal and additionally optionally ether groups and/or free hydroxy groups.

Preferably, the metal salt of trifluoromethane sulphonic acid has the following structure

$$(CF_3SO_3)_m\, M\, (OR)_n$$

wherein

(m+n) in total correspond to the valency of the metal cation and m is at least 1, m preferably corresponding to the valency of the metal,

R is a hydrocarbon radical with 1 to 28, preferably 2 to 8, carbon atoms which optionally comprises 1 to 8 ether groups, in particular 1 to 3 ether groups and/or 1 to 4 hydroxy groups,
is hydrogen, preferably, insofar at least one R is not hydrogen and R can be different for each n and

M is Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Sc, Y, La, Ti, Zr, Fe, Cu, Ag or Zn, preferably Al, Ti or Zr.

According to the process of the invention, metal triflates of high purity can be produced in a surprisingly simple manner in the dissolved state or as solid pure substance by adding CF_3SO_3H to metal alkoxides. Alcohol which is released is driven out after or during the addition of the trifluoromethane sulphonic acid.

The target substance can be removed from the reaction mixture by extraction with water. In contrast, the metal triflates exhibiting at least one alcohol group are frequently water insoluble in the case of a chain length of more than 4 of the carbon atoms of the alcohol group and can thus be separated from the water-soluble product and/or excess alcohol. Alcohol formed in the hydrolysis or alcohol used as diluent can be separated off by phase separation if water insoluble alcohols are involved (>= C4, preferably >= C5).

According to a further object of the invention, the metal triflates, as described above, among other things, can be used as catalysts for the synthesis of hydroxycarboxylic acid esters by conversion of hydroxycarboxylic acids with alcohols and/or transesterification.

Numerous routes for producing hydroxycarboxylic acid esters, in particular lactic acid esters, have been described. One variation is the direct esterification of hydroxycarboxylic acid with alcohols at elevated temperature without an addition of catalyst according to EP 0 287 426. In this case, the conversion is carried out at temperatures of 90 to 140 °C using alcohols with up to twelve carbon atoms for the preparation of optically active lactic acid esters. Since this process is merely quasi-continuous, the amount of equipment required is large.

Currently, proton-acidic or Lewis-acidic catalysts are used for the esterification process. These catalysts are frequently protonic acids such as hydrochloric acid, sulphuric acid, phosphoric acid, methane sulphonic acid, *p*-toluene sulphonic acid or acidic ion exchangers. Apart from the protonic acids, which frequently cause problems by corrosion, Lewis acids are also known as esterification catalysts, e.g. using metal halides or strongly acidic styrene resin in combination with the Lewis acid $AlCl_3$.

In the case of most esterification processes known from the state of the art, the water formed in the reaction is removed from the reaction mixture by azeotropic distillation by means of an entrainer. For this purpose, aliphatic and aromatic hydrocarbons are usually used.

Surprisingly enough, it has been found that hydroxycarboxylic acid esters can be obtained by the direct esterification of hydroxycarboxylic acids with alcohols in the presence of metal triflate catalysts which, moreover, exhibit an unusually high activity. The reaction times are short even when small quantities of catalysts are used. Depending on the alcohol used, the reaction times are usually 5 to 14 hours.

According to a further embodiment of the invention, the metal triflates, as described above, are used as catalysts for the transesterification of hydroxycarboxylic acid esters.

The metal triflates with at least one trifluoromethane sulphonic acid group are, in this case, brought into contact with hydroxycarboxylic acid esters, preferably with heating, with an alcohol and/or a further hydroxycarboxylic acid ester. As a rule, alcohols are used with a higher boiling point than the alcohol bound in the ester such that the alcohol with a lower boiling point is driven out of the reaction mixture. In this case, Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Sc, Y, La, Ti, Zr, Fe, Cu, Ag or Zn, particularly preferably Al, Ti or Zr are preferably used as metal component of the metal triflates.

The alcohols and/or alcoholate groups used for the esterification and transesterification can be branched, straight chain, saturated, unsaturated, aromatic, primary, secondary or tertiary and exhibit preferably 1 to 28 carbon atoms and, if necessary, 1 to 8 ether groups or 1 to 5 further hydroxy groups. The reacted aliphatic

and aromatic hydroxycarboxylic acid esters contain at least one hydroxy group (-OH) and one carboxylic acid ester group (-COO-) respectively.

The esterification and transesterification can be carried out at temperatures of 60 to 250 °C and pressures of 0.05 to 40 bar. The molar ratio of the alcohol used to the ester groups of the hydroxycarboxylic acid ester used is preferably 0.5 to 2.0 and the catalyst is preferably used in an amount of 0.02 to 1.0 % by weight, based on the hydroxycarboxylic acid ester to be reacted.

The work-up of the hydroxycarboxylic acid ester produced by transesterification can take place by distillation at temperatures in the region of 60 °C to 250 °C and pressures of 1 hPa to 1013 hPa or by stripping with steam at temperatures of 120 °C to 200 °C and pressures of 1 hPa to 1013 hPa, it being possible for the work-up to take place either directly from the raw product or after removing the catalyst and filtering the raw product. In the case of a work-up by distillation, the catalyst can be removed by adsorption with activated carbon, aluminium hydroxide or aluminosilicate before distillation or remain in the bottom product and be recycled into the process.

Catalysts which are used in the esterification reactions can also be used as catalysts for transesterifications.

The metal triflates are easy to handle and without problems both in the pure form and in solution. The compounds are stable and pose no particular requirements regarding storage. During handling, the usual measures for handling irritant substances need to be complied with. High yields of hydroxycarboxylic acid esters are achieved with a simultaneously high selectivity, the usual by-products such as the oligo and poly(hydroxycarboxylic acid) esters formed by the reaction of hydroxycarboxylic acids with each other, being formed in much lower proportions compared with the use of conventional catalysts. Moreover, they can be recycled into the reaction in order to be reesterified with an excess of alcohol to form simple hydroxycarboxylic acid esters.

A great advantage of the metal triflates compared with the protonic acids as catalyst is the low tendency to corrosion. It is by a factor of > 10 lower than that of a reaction mixture with the same proportion of sulphuric acid as catalyst.

The metal triflates can be produced in a simple manner as solids or in solution by reacting the acid with a metal alcoholate, as described above. In this respect, it is particularly advantageous that reaction products which have not been purified and contain e.g. suitable alcohols can also be used directly in the esterification reaction.

However, other processes are also known according to which aluminium salts or rare earth metal salts of trifluoromethane sulphonates are available, e.g. from the corresponding metal carbonates according to US 4,219,540 already cited above.

The metal triflates have a high Lewis acid activity and are stable in aqueous media. They can therefore be considered for use for numerous organic reactions in which water is contained in the starting materials, is formed as reaction product or used as solvent and/or in micro-emulsions. Thus, the metal triflates according to the invention are generally suitable in particular for reactions in protic media.

Hydroxycarboxylic acids according to the meaning of this invention are hydroxycarboxylic acids which contain at least one alcohol function (-OH) and one carboxylic acid function (COOH, including COO).

For the present invention, the following hydroxycarboxylic acids, are suitable in particular as compounds obtained from raw materials both for the esterification reaction and the transesterification reaction: glycolic acid, lactic acid,. β-hydroxy propionic acid, α-hydroxybutyric acid, β-hydroxybutyric acid and γ-hydroxybutyric acid, malic acid, tartaric acid, citric acid, mandelic acid and salicylic acid.

These hydroxycarboxylic acids are reacted with primary, secondary and tertiary, straight chain and branched alcohols with a chain length of 1 of 28 carbon atoms. Metal salts of trifluoromethane sulphonic acid (triflates) are used as catalysts. The following are used as metals: Li, Na, K, Ba, Mg, Ca, Al, In, Sn, Sc, Y, La, Ti, Zr, Fe, Cu, Ag and Zn.

The hydroxycarboxylic acid esters of the above-mentioned acids have a variety of applications. The esters of lactic acid with ethanol and *n*-butanol (ethyl lactate and *n*-butyl lactate) are used, among other things, as environment-friendly additives in solvent formulations for paints and in purifier formulations for the semiconductor industry. In this case, they are used for removing photo resists from templates, for example. In addition, both esters have been approved by the FDA as additives in the

food industry. The esters of other alcohols with a higher number of carbon atoms are also used in these fields or in the cosmetics industry. Cetyl lactate, in particular, is used in the U.S.A. in a large number of cosmetic formulations. The esters of citric acid with alcohols and alcohol mixtures, in particular with 4 to 16 carbon atoms, are used mainly as plasticisers for polymers. The esters of other hydroxycarboxylic acids have potentially the same fields of application.

Example

A Production of metal triflates

The experiments were carried out in a 1000 ml reaction flask of glass equipped with a thermometer, a distillation attachment, dropping funnel and stirrer as well as a vacuum distillation device with cooling traps.

To remove the heat of reaction the reaction vessel was cooled by means of an ice bath.

Example A1: Production of aluminium tristrifluoromethane sulphonate in isotridecanol

21.44 g of aluminium triisopropylate and 193.86 g of isotridecanol were introduced into a reaction flask and 45.02 g of trifluoromethane sulphonic acid were metered in at room temperature (25 °C) with vigorous stirring within approximately 1 h by means of a dropping funnel.

The reaction vessel was cooled continuously such that the bottom temperature did not exceed 40 °C.

Subsequently, a vacuum of 100 mbar was applied and the product heated to 110 °C within approximately 45 minutes.

At the same time, the pressure was reduced to 50 mbar and the co-product isopropanol was removed by distillation. Aluminium tristrifluoromethane sulphonate $(CF_3SO_3)_3Al$ remained in the flask in solution.

Example A2: Production of aluminium tristrifluoromethane sulphonate in isopropanol

10.72 g of aluminium triisopropylate and 87.93 g of isopropanol were introduced into the reaction flask and 22.5 g of trifluoromethane sulphonic acid were metered in at room temperature (25 °C) with vigorous stirring within 1 h by means of a dropping funnel. The reaction vessel was cooled continuously such that the bottom temperature did not exceed 40 °C. Subsequently, the reaction mixture was stirred for 1 h at room

temperature. Aluminium tristrifluoromethane sulphonate $Al(CF_3SO_3)_3$ in isopropanol remained in the flask.

Example A3: Production of zirconium tetrakistrifluoromethane sulphonate in isotridecanol
40.2 g of zirconium tetra-n-butylate and 305.08 g of isotridecanol were introduced into the reaction flask, 60.03 g trifluoromethane sulphonic acid were metered in at room temperature (25 °C) with vigorous stirring within 1 h by means of a dropping funnel. The reaction vessel was cooled continuously such that the bottom temperature did not exceed 40 °C. Subsequently, the product was heated under vacuum of 100 mbar to 110 °C within 45 minutes. At the same time, the pressure was reduced to 50 mbar and the co-product n-butanol was removed by distillation. Zirconium tetrakistrifluoromethane sulphonate $Zr(CF_3SO_3)$ remained in the flask $_4$ in solution.

Example A4: Production of aluminium tristrifluoromethane sulphonate, solvent free.
21.4 g of aluminium triisopropylate and 64.4 g of xylene were introduced into the reaction flask and heated in a rotary evaporator under a vacuum of 500 mbar to 70 °C. 45.0 g of trifluoromethane sulphonic acid were added within 60 min. and xylene and the co-product isopropanol were drawn off at 98 °C and 400 mbar.
Aluminium tristrifluoromethane sulphonate $Al(CF_3SO_3)_3$ remained in the flask as a solid. By means of AAS, metal impurities were determined which were below the limit values indicated in the introduction to the description.

B Production of hydroxycarboxylic acid using metal triflate catalysis

Production of lactic acid esters (lactates)
In the following, it is described how hydroxycarboxylic acids can be obtained be the direct conversion of hydroxycarboxylic acids with alcohols using metal triflates as catalysts. In this process, either the alcohol or the acid was used in excess (up to 100 %).
The water formed in the reaction was removed from the reaction mixture by azeotropic distillation using an entrainer. Aliphatic and aromatic hydrocarbons or dialkyl ethers were used as entrainers.
The reactions for the production of the lactic acid esters were carried out in a 2 l glass flask equipped with a column (Sulzer packing of stainless steel), a capillary for the introduction of nitrogen, a dropping funnel and a PT100 heat sensor. At the top of the column was a water separator with a reflux condenser. A heating dome was used for

heating. The reaction conditions employed were within a temperature range of 40 to 180 °C and a pressure range of 0.,2 to 10 bar, depending on the alcohol used.

Example B1: Production of lactic acid ethyl ester
563.0 g of lactic acid (80 % by weight in water, i.e. based on lactic acid and used as an 80 % by weight solution in water), 460.7 g of ethanol and 2.3 g $Al(OTf)_3$ (in 9 g of isotridecanol, based on $Al(OTf)_3$ and used as a 20 % by weight solution in isotridecanol), were introduced into a reaction flask. The water separator was filled with diisopropyl ether which served as entrainer. A further 300 g of diisopropyl ether were introduced into the flask. The bottom was heated to 80 to 90 °C such that a good reflux was formed and forming water was removed azeotropically at a head temperature of 62 °C. The course of the reaction was monitored by way of the acid number. The esterification was carried out up to an acid number of < 2 mg KOH/g. This was reached after 12 h, whereby a conversion of more than 99 % had been reached for the hydroxycarboxylic acid.

The yield of ethyl lactate was more than 88 %. The di-lactic acid ethyl ester was formed in a yield of 11 %.

The crude product was neutralised with $Ca(OH)_2$ to remove the residual acid and the catalyst and filtered. The entrainer and excess alcohol were removed by distillation from the filtrate and the crude product was subjected to fractional distillation at reduced pressure.

Example B2: Production of lactic acid ethyl ester
563.0 g of lactic acid (80 % by weight in water) were introduced into a reaction flask and part of the water was removed at reduced pressure at elevated temperature within 30 min such that the lactic acid was present as an approximately 95 % solution. 460.7 g of ethanol and 2.,3 g of $Al(OTf)_3$ (in 9 g of isotridecanol) were added.

The water separator was filled with diisopropyl ether which served as entrainer. A further 300 g of diisopropyl ether were introduced into the flask and the bottom was heated to 80 to 90 °C such that a good reflux was formed and the water generated was removed azeotropically at a head temperature of 62 °C. The course of the reaction was monitored by way of the acid number.

The esterification was carried out up to an acid number of less than 2 mg KOH/g. This, including drying of the lactic acid, was achieved after 9.5 h. The conversion of lactic acid was more than 99 %. The yield of ethyl lactate was more than 87 %, the dilactic acid ethyl ester was formed in a 12 % yield. The work-up of the crude product was carried our in a manner analogous to example B1.

Example B3: Production of lactic acid butyl ester
563.0 g of lactic acid, based on lactic acid and used as an 80 % by weight solution in water, 741.2 g of *n*-butanol and 2.3 g of $Al(OTf)_3$ (in 9 g isotridecanol) were introduced into the reaction flask. The water separator was filled with diisopropyl ether which served as entrainer. A further 300 g of diisopropyl ether were introduced into the flask. Tottom was heated to 90 to 120 °C such that a good reflux was formed and the water generated was removed azeotropically at a head temperature of 66 °C. The course of the reaction was monitored by way of the acid number and the esterification was carried out up to an acid number of less than 2 mg KOH/g. This was reached after 6 h whereby a conversion of more than 99 % was reached for the hydroxycarboxylic acid. The yield of ethyl lactate was more than 95 %, the dilactic butyl ester was formed in a yield of approximately 4 %. The work up of the crude product was carried out in a manner analogous to example B1.

Production of citric acid esters (citrate)
The reaction for the production of citric acid esters was carried out in a 2 l glass flask equipped with a column (Raschig rings of stainless steel), a capillary for the introduction of nitrogen, a dropping funnel and a PT100 heat sensor. A water separator with a reflux condenser was fitted to the head of the column. A heating dome was used for heating. The reaction temperature was in the range of 80 to 180 °C and a pressure range of 0.2 to 2 bar.

Example B4: Production of a citric acid ester with a mixture of linear C6/C8 alcohols, catalyst $Al(OTf)_3$
384.2 g of citric acid, 1048.4 g of C6/C8 alcohol and 1.2 g of $Al(OTf)_3$ (in 4.5 g of isotridecanol) were introduced into a reaction flask. The alcohol served simultaneously as entrainer for the water. The bottom was heated to 110 °C at reduced pressure such that a good reflux was formed and the water generated was removed azeotropically at a head temperature of 80 °C.

The course of the reaction was monitored by way of the acid number and esterification was carried out up to an acid number of 0.6 KOH/g which was reached after 9 h.

The conversion of citric acid was thus greater than 99 %. The reaction mixture was dissolved with an equimolar quantity of NaOH, based on the acid number, neutralised in 1 % water (based on the amount weighed in) for 20 min at 40 °C and subsequently dried for 15 to 20 min at reduced pressure and temperature of up to 80 °C. To remove the excess alcohol, the crude product was stripped in a laboratory stripping apparatus using steam at 135 to 195 °C.

Example B5: Production of a citric acid ester with a mixture of linear C6/C8 alcohols, catalyst, $Zr(OTf)_4$
864.5 g of citric acid, 2358.8 g of C6/C8 alcohol and 1.3 g of $Zr(OTf)_4$ (in 5.1 g of isotridecanol) were introduced into a reaction flask. The alcohol served simultaneously as entrainer. The bottom was heated to 110 °C at reduced pressure such that a good reflux was formed and the water generated was removed azeotropically at a head temperature of 80 °C. The course of the reaction was monitored via the acid number and continued up to an acid number of 0.6 mg KOH/g which was reached after 14 h. The conversion of citric acid was thus more than 99 %. The work-up was carried out in a manner analogous to example B4.

Example B6: Production of a citric acid ester with a mixture of linear C6/C8 alcohols, catalyst, $Sn(OTf)_2$
384.2 g of citric acid, 1048.4 g of C6/C8 alcohol and 0.1 g of $Sn(OTf)_2$ (in 0.4 g of isotridecanol) were introduced into a reaction flask. The alcohol served simultaneously as entrainer. The bottom was heated to 135 °C at reduced pressure such that a good reflux was formed and the water generated was removed azeotropically at a head temperature of 100 °C. The course of the reaction was monitored via the acid number and continued up to an acid number of 0.5 mg KOH/g which was reached after 5 h. The conversion of citric acid was thus > 99 %. The work-up was carried out in a manner analogous to example B4.
The apparatus for the production of the tartaric ester and malic acid ester corresponded to that used for the production of citric acid ester.

Example B7: Production of tartaric acid dialky ester with C6/C8 alcohol

450.3 g of tartaric acid, 1084.5 g of C6/C8 alcohol and 1.8 g of $Al(OTf)_3$ (in 7.2 g of isotridecanol) were introduced into the flask. The water separator was filled with cyclohexane which served as entrainer.

Further cyclohexane was introduced into the flask. The bottom was heated to 80 to 120 °C at reduced pressure and the water ghenerated was removed azeotropically. The course of the reaction was monitored by way of the acid number and continued up to an acid number of < 1 mg of KOH/g which was reached after 8 to 10 h, corresponding to a conversion of 99 % with respect to the hydroxycarboxylic acid. The work up was carried out in a manner analogous to example B4.

Example B8: Production of malic acid dialkyl ester with C6/C8 alcohol

402.3 g of malic acid, 1084.5 g of C6/C8 alcohol and 1.6 g of $Al(OTf)_3$ (in 6.4 g of isotridecanol) were introduced into a reaction flask. The water separator was filled with cyclohexane which served as entrainer. Further cyclohexane was introduced into the flask and the bottom was heated to 80 to 120 °C at reduced pressure and the water generated was removed azeotropically. The course of the reaction was monitored by means of the acid number and esterification was carried out up to an acid number of less than 1 mg of KOH/g. This was reached after 8 to 10 h as a result of which a conversion of more than 99 % was reached for the hydroxycarboxylic acid. The work up took place in a manner analogous to example B4.

Transesterification of lactic acid esters (lactates)

In the following examples, conversions are described according to which hydroxycarboxylic acid esters are reesterified in the presence of metal triflates as catalysts and alcohols. In this process, the alcohol is used in excess (up to 100 mole %). The lower boiling alcohol liberated in the reaction is removed from the reaction mixture by distillation.

The reactions for the transesterification of lactic acid esters were carried out in a 1 l glass flask equipped with a column (filled with 6 mm Raschig rings) and a column head, a capillary for the introduction of nitrogen and a PT100 heat sensor. A heating dome was used for heating. The reaction conditions used were in a temperature range of 60 to 240 °C and a pressure range of 0.05 to 10 bar.

Example C1: Transesterification of lactic acid ethyl ester with n-butanol und $Al(OTf)_3$

118.1 g (1.0 mole) of ethyl lactate and 148.2 g (2.0 mole) of n-butanol were introduced into the flask and 0.6 g (2.5 mmole) of $Al(OTf)_3$ were added as a 20 % solution in n-butanol. The reaction mixture was heated to approximately 120 °C. The ethanol formed in the reaction was withdrawn overhead. In the course of the reaction, the bottom temperature was raised stepwise up to approximately 140 °C.

The increase in the head temperature from the boiling point of pure ethanol to the boiling point of pure n-butanol indicated the end of the reaction. The course of the reaction was additionally monitored by GC. For the work-up of the crude product, the catalyst was removed by means of an adsorption agent and the crude product was filtered.

Subsequently, a distillative separation of the excess alcohol and fractional distillation of the reaction product were carried out.

Time (h)	1.5	3.0	4.5	6.0
Conversion of ethyl lactate (%)	75.8	97.1	99.8	99.9
Yield of n-butyl lactate (%)	70.9	89.9	90.8	89.5
Yield of oligomeric esters (%)	4.9	7.2	9.0	10.4
Selectivity %	93.5	92.6	91.0	89.5

Example C2: Transesterification of lactic acid ethyl ester with n-butanol and $Zr(OTf)_4$

118.1 g (1.0 mole) of ethyl lactate and 148.2 g (2.0 mole) of n-butanol were introduced into the flask and 0.6 g (1.8 mmole) of $Zr(OTf)_4$ were added as a 20 % solution in n-butanol. The reaction mixture was heated to approximately 120 °C. The ethanol formed in the reaction was withdrawn overhead. In the course of the reaction, the bottom temperature was raised stepwise up to approximately 140 °C.

The increase in the head temperature from the boiling point of pure ethanol to the boiling point of pure n-butanol indicated the end of the reaction. The course of the reaction was additionally monitored by GC.

Time (h)	1.0	2.0	3.0	6.0
Conversion of ethyl lactate (%)	50.9	78.4	93.5	99.6
Yield of n-butyl lactate (%)	46.6	73.6	87.7	90.4
Yield of oligomeric esters (%)	4.3	4.8	5.8	9.2
Selectivity %	91.6	93.8	93.8	90.8

Example C3: Transesterification of lactic acid ethyl ester with isopropanol $Al(OTf)_3$

118.1 g (1.0 mole) of ethyl lactate and 120.2 g (2.0 mole) of isopropanol were introduced into the flask and 0.6 g (2.5 mmole) of $Al(OTf)_3$ were added in the form of a 20 % solution in isopropanol. The reaction mixture was heated to approximately 90 °C. The ethanol formed in the reaction was withdrawn overhead. In the course of the reaction, the bottom temperature was raised stepwise up to approximately 105 °C. After 6½ hours, the conversion of ethyl lactate was approximately 25 %. This lower rate of reaction is attributable above all to the lower reaction temperature and the difficult distillative separation of the ethanol as a result of the slight difference in the boiling point with respect to isopropanol.

Example C4: Transesterification of lactic acid isopropyl ester with n-butanol and $Al(OTf)_3$

132.2 g (1.0 mole) of isopropyl lactate and 148.2 g (2.0 mole) of n-butanol were introduced into the flask and 0.66 g (2.8 mmole) of $Al(OTf)_3$ were added as a 20 % solution in n-butanol. The reaction mixture was heated to approximately 125 °C. The isopropanol formed in the reaction was withdrawn overhead. In the course of the reaction, the bottom temperature was raised stepwise up to approximately 145 °C. The increase in the head temperature from the boiling point of pure isopropanol to the boiling point of the pure n-butanol indicates the end of the reaction. The course of the reaction was additionally monitored by GC.

Example C5: Transesterification of citric acid tri-n-butyl ester with 1-hexanol and $Zr(OTf)_4$

360.5 g of citric acid tri-n-butyl ester, 625.1 g of 1-hexanol and 1.8 g of $Al(OTf)_3$ (20 % in isotridecanol) were introduced into the flask. The reaction mixture was heated to approximately 150 °C. The n-butanol formed in the reaction was withdrawn overhead. The bottom temperature was increased stepwise in the course of the reaction to as much as approximately 180 °C. To remove the excess alcohol, the crude product was stripped in a laboratory stripping device using steam at 135 to 195 °C.

Example C6: Transesterification of diisopropyl tartrate with 1-hexanol and AL(OTf)$_3$ 234.3 g (1.0 mole) of diisopropyl tartrate (416.8 g of 1-hexanol (4.0 mole) and 1.17 g of Al(OTf)$_3$ (20 % in isotridecanol) were introduced into the flask. The reaction mixture was heated to approximately 100 ^{0}C. The i-propanol formed in the reaction was withdrawn overhead. The bottom temperature was increased stepwise in the course of the reaction to as much as approximately 120 ^{0}C. To remove the excess alcohol, the crude product was stripped in a laboratory stripping device using steam at 135 to 195 ^{0}C.